Panel Discussion on

Commentary article

ULI OSTERWALDER

Uli Osterwalder is Principal and Owner of the Sun Protection Facilitator GmbH in Basel, Switzerland (www.sunprotection.co). Before starting his own consulting company, which is committed to contribute to further improvements in sun protection, Uli Osterwalder worked in Personal Care for 20 years. He is also an expert at ISO on the development of new UV protection test methods since 2006 and is now the chairperson of the technical committee on Cosmetics (ISO TC 217). He is author and co-author of numerous scientific articles and book chapters on sun protection, co-initiator of the "ALT-SPF Consortium" (www.alt-spf.com), and also co-editor of the series of papers on Challenges in Sun Protection in Current Problems in Dermatology, published by KARGER, Basel in 2021.

TOPICS OF THE DISCUSSION

The 13 contributions to the panel discussion can be grouped into four themes that cover some current challenges in sun protection:

1) The Formulator's Challenge
   How to create safe sunscreens – for people and the environment.
2) What Wavelengths to Protect Against?
   Should we go beyond UV protection?
3) Impact of Sunscreens on the Environment
   Sunscreen impacts on marine life: challenges and future perspectives
4) Meeting Consumer Expectations
   Understanding consumer expectations to formulate efficient suncare products

1. THE FORMULATOR'S CHALLENGE

How to create safe sunscreens – for people and the environment.

Tony Gough and Alice Mile from Innospec emphasise the important role of emollients in sunscreens. When formulating with organic UV-filters, it is important to ensure that all solid filters are sufficiently solubilised. If recrystallisation occurs, it can feel scratchy on the skin, lead to emulsion instability and reduce the amount of UV protection provided. Therefore, it is critical that sufficient polar emollients are used as solvents to ensure that the solid UV-filters are adequately solubilised. Although there are challenges in formulating sunscreens with high levels of organic or inorganic filters, these can be overcome with the right emollients and/or dispersants to ensure that high-performance formulations with good stability and excellent feel can be achieved.

Myriam Sohn from BASF reminds us that nano-particulate UV filters offer many advantages for formulators and consumers. Nano-sized UV filters do not need to be dissolved. By replacing some oil-soluble filters with nanofilters, the amount of emollients required to dissolve lipophilic solid UV filters can be reduced, making formulations lighter.

Natércia das Neves Rodrigues Lopes and Juan Cebrian from Lubrizol explain how ultrafast laser spectroscopy techniques contribute to the future of suncare. The future of suncare is likely to lie in such questions. The key to the ideal sunscreen lies in understanding the ultrafast molecular behaviour of sunscreen filters after irradiation, known as photodynamics, which can only be studied using state-of-the-art ultrafast laser spectroscopy techniques.

Laura Busata from Unifarco explains that the effectiveness of a sunscreen is the result of a precise formulation design that combines the absorbing properties of the filters with the selection of emulsifiers, lipids and polymers capable of ensuring the uniformity and convenience of application necessary for sun protection under real product application conditions. The right balance of ingredients can be evaluated using techniques such as rheology and texture analysis, which are useful tools to optimise the sunscreen's properties and meet consumer needs.

COMMENT:

Supplier expertise is very valuable as sunscreen manufacturers do not reveal their secrets. Suppliers, of course, also want to sell their ingredients. Measuring the photodynamics of sunscreens will remain important to test new formulation platforms as some well-established agents for photostabilising formulations disappear, e.g. octocrylene, and at the same time the traditional SPF method will eventually be replaced by non-invasive alternatives that do not directly consider photostability. We need to ensure that sunscreen formulations continue to be photostable. Nanoparticulate UV filters may well be the future, once concerns about "different behaviour from bulk material" are investigated and addressed.

SUN PROTECTION

Experts were invited to discuss trends and relevant aspects of Sun Care. Some topics of the panel discussion are highlighted and commented by Uli Osterwalder, Sun Protection Facilitator GmbH.

The fact is that nanoparticulate UV filters are much larger than the dissolved single molecules of conventional organic UV filters, which are known to be absorbed to some extent.

2. WHAT WAVELENGTHS TO PROTECT AGAINST?
Should we go beyond UV protection?

Olga Dueva-Koganov from Intellebio illustrates that the intensity of Blue Light emitted by the Sun is about 2 to 3 orders of magnitude greater than that emitted by electronic devices. The experimental data she presented once again underlines the importance of comprehensive sun protection in the areas of UVB/UVA, blue light, VIS and NIR. The development of multifunctional sunscreen formulations capable of providing measurable protection beyond the UV range is a challenging task that requires the development and use of specific ingredients and formulations, as well as relevant test methods and metrics, such as blue light to UV ratios.

Joseph Peake from Croda also argues that we should go beyond UV protection. Visible light, including HEV light, has lower energy than UV but can penetrate deeper into the skin than both UVA and UVB and can contribute to age-related macular degeneration by activating metalloproteinases that promote the breakdown of collagen and elastin, causing glycation folds and premature ageing. Electron spin resonance (ESR) is an in vitro testing method that uses an electron trap to extend the lifetime of radicals generated by exposure to sun-simulated radiation, which facilitates the detection of radical species.

Maria Barbero from Zurko elaborates on the SPF gold standard ISO 24444:2019. The starting point to evaluate each sunscreen product is through the traditional gold standard ISO 24444 (or the similar FDA method). The first edition of this procedure: ISO 24444:2010 has recently been replaced by the second edition ISO 24444:2019. It is important to bear in mind that the ISO 24444:2019 will continue to be under development.

Christian Surber from the University of Zurich and Uli Osterwalder from Sun Protection Facilitator explain the terminology and emphasise the approach to validating alternative SPF and UVA-PF methods. Once suitability and equivalence between reference/gold standard and alternative methods have been established, each of the methods can be used - comparable to tools from a toolbox - to reliably assess a more holistic protective performance of sunscreens. Such methods, complementing each other, would be a significant advance in the development and application of sunscreens.

COMMENT:
Originally, sun protection started as UVB protection, then a minimum of UVA protection was required and now VIS/blue light protection is recommended. The need for IRA protection is not yet proven, IRA might even be beneficial rather than harmful, some argue. In the meantime, we should not forget UVA protection. There is still much room for improvement here.

The idea that the emission of blue light from electronic devices could somehow damage the skin has been debunked. What remains, of course, is its effect on melatonin breakdown via the eyes. So, any damage to the skin from blue light would come from the sun. Covering the blue area is tricky; many users don't want to look white. The question remains how well we need to protect ourselves from VIS/blue light; a protection factor of 2-3 might actually be sufficient. The SPF gold standard remains the basis of sun protection, but it will need to be revised to include protection against the real sun.

3. IMPACT OF SUNSCREENS ON THE ENVIRONMENT
Sunscreen impacts on marine life: challenges and future perspectives

Roberto Danovaro and Cinzia Corinaldesi from the Polytechnic University of Marche, Italy discuss the impact of sunscreen on marine life. Among the thousands of contaminants released in the sea, there is increasing evidence that sunscreens despite their extremely low concentrations can have disproportionately high impacts on a large variety of aquatic organisms. Consequently, the ban for some ingredients such as the octinoxante and oxybenzone is planned or already adopted in some countries.

Jody Jourden from EverCare, representing a trusted zinc oxide supplier, is campaigning through her Positive Reef Initiative to fully understand and present the actual effects of UV filters, particularly zinc oxide, on aquatic life in general and corals in particular. As regulations have continued to restrict the use of sunscreens, attention has focused on zinc oxide (ZnO) as the UV filter of choice in the development of reef-friendly sunscreens, but this attention has also led to misinformation among the public about the true environmental impacts of ZnO.

BASF's Myriam Sohn explains from the perspective of a UV filter expert what can be done today to evaluate UV filters. The BASF EcoSun Pass value is based on eight different parameters, i.e. acute and chronic aquatic toxicity, bioaccumulation and biodegradability.

This allows our customers to evaluate their sunscreen products based on all relevant environmental factors and bring the most environmentally friendly consumer product to the market.

COMMENT:
Roberto Danovaro and his group were the pioneers of work on the impact of sunscreen on marine life. Their first paper in 2008 got a lot of attention in the Cosmetics Industry. But it took almost a decade until things started moving, after an article of Craig Downs et al that led to a ban of certain UV filters in Hawaii. Now, to be up to date one has to check the literature on a monthly basis. But we should avoid throwing the baby out with the bathwater, therefore a proper risk assessment/management approach is required, e.g., ZnO is an essential element and there is a background concentration in the sea. The hazard warning for bulk transport of ZnO must not be misinterpreted as risk analysis.

4. MEETING CONSUMER EXPECTATIONS

Understanding consumer expectations to formulate efficient suncare products

Flora Bollon from Gattefossè emphasizes sensoriality as a key factor to ensure that the product will be appreciated, applied and reapplied and therefore effective. Formulating a sensorial suncare product is not an easy task. Organic UV filters bring greasiness, a high film residue and tackiness. Inorganic UV filters can bring dryness, roughness and a whitening effect especially and a high amount of oil phase is needed to solubilize or disperse UV filters, that can lead to a greasy and heavy afterfeel.

Ingrid Vervier from DOW explains that in response to the desire for product safety and transparency, Dow has developed a brand-new bio-based and readily biodegradable SPF booster that enables higher SPF efficiency in sun care and daily skincare. Dow's new innovative microcrystalline cellulose is derived from PEFC certified pulp and supports the market demand for natural formulations.

Jürgen Vollhardt from DSM answers the often-heard question whether sunscreens block the positive aspects of sun exposure? Clearly no! In general, sunscreens are under-applied and this reduced application also reduces the protection against UVB and UVA light. In any case, the protection factor for UVA is typically three times lower than SPF. This is regulated by the manufacturers of the claims. For example, at an application concentration of 0.4 mg/cm2, a lotion with SPF 30 can be expected in practice to achieve an SPF of only 6 on the beach. In all circumstances, the use of sunscreen requires a certain tolerance to the application of a somewhat greasy product. And not every consumer is willing to use sunscreen. About 20% of consumers worldwide do not use sunscreen at all, and a significant number of consumers use sunscreen only on specific occasions.

COMMENT:
Asking consumers is a very good idea in marketing, but consumers do not know all the details of the technology and the challenges, so we also need to try to give them guidance on proper sun behaviour and their perception of sunscreens. The goal of sun protection is obvious, but apparently not for everyone; many apply too little sunscreen, too late or not at all. This is similar to vaccine hesitancy, except that applying sunscreen is a much more complex setting than vaccinating, for example, against measles or Covid-19. Education is the key.

Panelists

THE FORMULATOR'S CHALLENGE

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THE FORMULATOR'S CHALLENGE

HOW TO CREATE SAFE SUNSCREENS - FOR HUMANS AND THE ENVIRONMENT

Sunscreens and UV filters contribute significantly to human health by helping to protect the skin against the harmful effects of UV radiation, such as erythema, premature skin ageing, age spots and – with frequent intensive exposure – an increased risk of skin cancer. Although their benefits are uncontested, sunscreens and UV filters are subject to broad, often controversial public debate, not least on social media channels, regarding their safety for the human body as well as the environment. While many bloggers and journalists are well informed about cosmetics, there is still much false or scientifically unsubstantiated information circulating about cosmetic ingredients in general and UV filters specifically. Over the past few years, for example, the reputation of nano-particulate UV filters has been adversely affected by negative publicity in the press and by consumer apps. This has led to increasing concerns among consumers regarding the safety of nano-particulate UV filters. Although they have undergone a complex registration process attesting to their safety of use on humans, some sunscreen manufacturers prefer to follow non-scientific-based opinions and remove them from their formulations, thus losing all the valuable benefits of this category of UV filters.

According to the European Commission's definition, the term nanomaterial means "(…) materials containing particles (…) where, for 50 percent or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm". In other words, particulate nanofilters are classified as 'nano' exclusively due to their particle size.

There are currently four nanofilters approved for use in the European market: zinc oxide (ZnO) and titanium dioxide (TiO2), which are inorganic, and methylene bis-benzotriazolyl tetramethylbutylphenol (MBBT) and tris-biphenyl triazine (TBPT), which are organic. While there is widespread fear that nanofilters have the potential to penetrate the skin, percutaneous absorption depends not only on the particle size of the molecule but on several other properties such as chemical structure, molecular weight, solubility, polarity and melting point. It is extremely unlikely that the organic and inorganic nanofilters in our portfolio will penetrate the skin. With particle sizes ranging between 20 and 500 nanometers, they are much larger than soluble UV filters. Compared to them, nano particulate UV filters are big.

It is important to note that nano-particulate UV filters offer many advantages for formulators and end consumers. The efficacy of nano-particulate UV filters depends on the particle size, with absorption increasing as the particle size decreases. Moreover, due to their particulate nature they reflect and scatter light. The organic nanofilters (MBBT and TBPT) combine both the high absorbance of the soluble organic filters with the excellent light-scattering ability of the inorganic filters which makes them unique in terms of performance. Beyond the positive impact on efficacy, nano particles also have a reduced white painting effect.

Nano-sized filters do not need to be dissolved. Replacing some oil-soluble filters with nanofilters allows for a reduction in the amount of emollients required to dissolve lipophilic solid UV filters, which makes formulations lighter. Additionally, it becomes easier to formulate sunscreens with a high SPF. Moreover, the use of highly efficient UV filters requires low-use concentrations to be able to develop optimized sunscreens; this can also have a positive ecological effect on the final formulation.

This brings us to another key driving factor in the sun care industry: eco-sustainable sunscreens. Eco-conscious consumers are increasingly looking for more sustainable products offering improved environmental compatibility. Public discussion focuses primarily on the damage UV filters may cause to ecosystems, given that they tend to be released directly into the environment. To assess the environmental impact of the UV filters used in sunscreen formulations, BASF has developed the EcoSun Pass® approach. This methodology supports the transparent, holistic assessment of UV filters based on internationally recognized criteria and provides a comprehensive environmental evaluation of the entire filter system within a sunscreen product. The EcoSun Pass® value is based on eight different parameters, i.e. acute and chronic aquatic toxicity, bioaccumulation and biodegradation. This enables our customers to evaluate their sunscreens based on all the relevant environmental factors and allows the most eco-friendly consumer product to be brought onto the market.

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CHALLENGES IN FORMULATING SUNSCREENS - FORMULATING PRODUCTS WITH MINERAL ONLY SUNSCREENS, WITH ORGANIC SUNSCREEN ACTIVES, OR THEIR COMBINATIONS

Formulating sunscreens is notoriously challenging. Achieving a stable formulation with high enough sun protection can be difficult. The need for higher SPF and UVA protection is increasing as consumers become more aware of the damage the sun can do to their skin. This means higher and higher levels of actives are needed. This can cause a number of issues to overcome in order to achieve a stable formulation.

When formulating with organic UV-filters it is important to ensure that any solid filters are sufficiently solubilised. If any re-crystallisation occurs it can feel scratchy on the skin, cause emulsion instability and reduce the amount of UV protection offered. Therefore, it is critical to make sure that sufficient polar emollients are used as solvents to ensure that the solid UV-filters are adequately solubilised.

Benzoate esters have a long history of being used as UV-filter solvents. They have excellent hydrolytic and thermal stability along with low colour and odour. The following key benzoate esters are offered by Innospec:

- C12-15 Alkyl Benzoate, the most widely used and versatile grade.
- A new C12-15 Alkyl Benzoate grade with 28% naturally derived renewable content which maintains the excellent stability and solvency properties but allows formulators to increase the natural content of their formulation.
- Dipropyleneglycol Dibenzoate, optimised for even higher solubilising power.
- A blend of C12-15 Alkyl Benzoate, Dipropylene Glycol Dibenzoate and PPG-15 Stearyl Ether Benzoate optimised for a combination of good solubilisation power along with an elegant feel on the skin both during and after application.

Innospec also offers Diethylhexyl Maleate which is an aliphatic ester, but also offers excellent solubility for solid organic UV-filters and elegant skin feel.

A comparison of individual emollients for their solvency capacity with individual solid UV-filters can be done using a test to determine the level at which the solid precipitates. Solutions are prepared with heating and mixing at 80°C then cooled to room temperature. Precipitation is forced either through seeding and/or supersaturation. Four weeks is allowed for the sample to reach equilibrium after initial precipitation then the supernatant is tested via UV/Vis-spectroscopy to give the solvency capacity. Innospec's results for this are available upon request.

In a typical sun screen formulation, a number of UV-filters will be used in combination, along with liquid UV-filters which can themselves also dissolve solid UV-filters. It is also likely that more than one emollient will be used in the formulation. Nevertheless, the solvency data mentioned above still provide a useful indication of the relative suitability of the emollients for each filter.

When formulating with inorganic UV-filters there are again challenges to consider. Rather than being dissolved, the particles must be dispersed in the oil phase of the emulsion. Again, this is to avoid a scratchy feel on the skin, instability of the emulsion and reduction in UV properties.

Polyhydroxystearic Acid (PHSA) is a 100% naturally derived polymer that adsorbs to the surface of zinc oxide or titanium dioxide and ensures particles are well dispersed, and remain well dispersed, by steric repulsion between the particles. Innospec offers two grades which have the same INCI name but different molecular weights leading to slight differences in their physical properties. PHSA is an excellent dispersant to use for a popular combination for natural sunscreens: uncoated zinc oxide in caprylic/capric triglyceride.

A demonstration of the excellent dispersing power of these PHSA grades can be done by preparing a slurry of the powder and the oil by stirring with a dispersing head at 700-1000 rpm, and the initial viscosity measured. Incremental amounts of the PHSA are then added with stirring and the viscosity measured after each addition. The initial viscosity is high but drops sharply with increasing levels of PHSA indicating their excellent dispersing power. This allows high levels of zinc oxide to be included in formulations with excellent UV performance, pleasant feel and good stability over time.

Although there are challenges in formulating sunscreens with high levels of organic or inorganic filters, these can be overcome with the right emollients and/or dispersing agents to ensure that high-performing formulations with good stability and excellent feel can be achieved.

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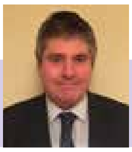

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THE ROLE OF SUNSCREEN PHOTODYNAMICS IN THE MOLECULAR DESIGN OF AN IDEAL SUNSCREEN FILTER

What is the role of sunscreen filters?

The main requirement for an ideal sunscreen filter is perhaps obvious: it must provide protection against harmful solar radiation. The portion of solar radiation most harmful to human skin is ultraviolet radiation, usually categorized into UV-B (280-315 nm) and UV-A (315-400 nm). The mechanisms of action for UV-B and UV-A damage are slightly different. UV-B, being a more energetic type of radiation, is directly absorbed by DNA and other important proteins in the skin, which can lead to direct damage, including DNA mutations that lead to skin cancer. UV-A radiation, on the other hand, is less energetic but much more abundant. UV-A also penetrates deeper into the skin, where it induces the generation of oxidant species that indirectly damage DNA, resulting most often in skin aging but also contributing to skin cancers.

The main role of a sunscreen filter is to absorb harmful UV-B and UV-A radiation, or to scatter it away, before it reaches skin cells. To date, chemical filters remain the most effective at achieving this goal. Molecules such as octocrylene, ethylhexyl methoxycinnamate and avobenzone – all common names to the suncare formulator – strongly absorb radiation in the UV-B and UV-A range, providing the necessary protection against these types of radiation. But it comes at a price: something must happen with the absorbed energy, and what does happen is not always good.

What do sunscreens do with the light they absorb?

The photostability of a sunscreen is usually measured by comparing the protection it provides before and after irradiation. The more the protection is maintained after irradiation, the better, but protection is almost never completely maintained. What happens in between? When a sunscreen filter absorbs radiation, it enters a high energy form of itself called a 'photoexcited state'. These high energy states are not stable, and the excess energy needs to be dissipated. In the case of avobenzone, for example, a famously photo-un-stable sunscreen filter, the energy absorbed induces degradation of the molecule and it breaks into several pieces. Other sunscreen filters instead dissipate energy by entering highly reactive states which can transfer energy to their surroundings. The interaction between these reactive states and oxygen in skin tissue, for example, generates oxidant species that cause damage to DNA and other biologically important molecules.

Ideally, a sunscreen filter would dissipate the energy it absorbs by shaking it away. In other words, the ideal sunscreen filter should dissipate absorbed energy through vibrating chemical bonds, which in chemistry terms means dissipating energy as heat. These energy dissipation processes must be very fast to ensure that excess energy has no chance of being transferred anywhere else, avoiding harmful side chemistry. In fact, these light-to-heat energy dissipation processes are known to take place on a femto- to picosecond timescale, that is, within 10^{-15} to 10^{-12} seconds.

Not all energy transfer processes are bad news, however. The effects of these processes are best demonstrated by the effect of combining different sunscreen filters. It is known that combining avobenzone with ethylhexyl methoxycinnamate leads to enhanced degradation post-irradiation, while adding octocrylene to the mix instead enhances photostability. These observations can be explained by the fact that each of the filters will have excess energy post-irradiation, and that they will be transferring this energy between themselves. But why does energy transfer between avobenzone and a cinnamate result in more degradation, while octocrylene has the opposite effect? What are the mechanisms of action at play? If we can understand them, can we mimic them to improve photostability of these and other sunscreen filters?

How can ultrafast laser spectroscopy techniques contribute to the future of suncare?

The future of suncare is likely to reside in these types of questions. The key to the ideal sunscreen is locked away in the understanding of the ultrafast molecular behaviors of sunscreen filters after irradiation[1], called their photodynamics, which can only be studied by state-of-the-art ultrafast laser spectroscopy techniques[2]. Understanding sunscreen photodynamics may also inform the molecular design of new filters[3] which are effective in providing solar protection while also being nontoxic to humans and to the environment. Having recognized the importance of a fundamental understanding of ultrafast sunscreen photodynamics, Lubrizol Life Science is actively involved in this field of research.

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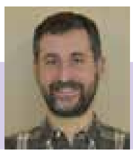

SAFE, EFFECTIVE AND SUSTAINABLE SUN CARE PRODUCT: A NEW FORMULATORS CHALLENGE

Sunscreens play a fundamental preventive role in the protection of health. Even today, many consumers identify in the SPF on the label the main indicator of the protection given by the product. However, people normally apply much less sunscreen than used in the testing process to determine a product's SPF (1). Sunscreen is normally spread hastily and not uniformly. This applies also to spray-on sunscreens if they are not rubbed in after application (2).

The absorbing property of the UV filters and the amount of applied product, the homogeneity of distribution of the sunscreen was found to play an important role with respect to SPF in vivo (3). The ideal situation for optimal performance is to achieve a film with uniform thickness, resembling the perfectly homogeneous distribution of a solution of UV filters in an optical cell (4).

Why do some consumers apply significantly less than the necessary amount of 2 mg/cm^2? There might be a multitude of answers. Certainly, however, the consumer's decision is influenced by the sensory aspects of the sunscreen. Sensory aspects can clearly influence the behavioral pattern in terms of the amount and frequency a consumer uses a sunscreen product and therefore sensory aspects need to be carefully controlled and optimized (5).

The effectiveness of a sunscreen is the result of a precise formulation design that combines the absorbent properties of the filters, with the choice of emulsifiers, lipids and polymers capable of ensuring uniformity and pleasantness of application, necessary for sun protection in real conditions of use of the product. The correct balance of the ingredients can be assessed using techniques such as rheology and texture analysis which represent a useful tool to optimize the properties of the sunscreen and meet the needs of consumers (6).

For this reason, new generation textures are very light and with an extremely thin and not heavy residue. This can be a double-edged sword in terms of long-term protection, indeed, the lighter is the product, the less persistent it is on the skin.

There is another aspect to take into account. The extremely watery textures are of course very pleasant on the skin, but they have a very high wash-off index and for this reason, a large amount of sun products could be released into the water.

One of the last big challenges for a formulator is understanding how to develop safe and effective sun care products, considering the great consumer's attention and awareness about their environmental impact, especially on the marine ecosystem.

The Clean Beauty concept is going to turn toward marine life and coral reefs integrity and Ocean Safe Beauty is one of the last born beauty trends, a sustainable and eco-friendly approach to product development, with a special focus on the respect of the marine ecosystem. How can we develop ocean safe products? There are different and at the same time linked directions to follow, starting from avoiding marine impacting ingredients, choosing more environmentally friendly packaging or reducing water wasting creating waterless cosmetics.

In recent years, a number of studies have shown that sunscreens and other cosmetic products contain chemical substances that are adding to the pollution burden faced by coral reefs (7).

There is intense concern about the future health and ecological integrity of coral reefs in the face of global climate change. Many studies have been carried out to investigate the occurrence and concentration of UV filters in seawater and marine sediment. To date, however, the level of exposure has only been quantified at a few coral reef sites. Where sunscreen components have been detected, concentrations are very variable and most work has been undertaken on oxybenzone (8) and further research is thus needed before firm conclusions can be reached.

This fact, however, must be a starting point for cosmetic companies, that have a chance of developing new effective and low impact formulas. For now, we do know that the removal of some chemicals such as Oxybenzone, Benzophenone-2, the camphor derivatives, EHMC and non-coated inorganic filters, would be positively beneficial to the ocean. In addition, reducing the levels of UV filters would be a start toward a solution. This could be achieved through the use of boosters to enhance protection without increasing the percentage of filters present in the formula. A direct and efficient way to reduce the release of sunscreen products on seawaters could be the formulation of water-resistant or very water-resistant products.

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WHAT WAVELENGTHS TO PROTECT AGAINST

SHOULD WE LOOK TO EXPAND BEYOND UV PROTECTION?

UV is undoubtedly the most important region of the solar spectrum to protect the skin from, with both UVA and UVB causing considerable harm in the form of erythema, skin photoaging and skin cancer, but that does not mean that we should not look at how other wavelengths can affect the skin. Of all the solar radiation that reaches the earth, only ~7% is in the form of UV, so let's look at some of the other wavelengths.

High energy visible (HEV) or blue light refers to wavelengths of radiation between 380 nm and 500 nm and is a part of the visible light region. This accounts for ~ 39% of incident solar radiation and has been shown to have demonstrable effects on human cells (1). Visible light, including HEV light, whilst having lower energy than UV, can penetrate deeper into the skin than both UVA and UVB and can contribute to age-related macular degeneration by activating metalloproteinases to promote degradation of collagen and elastin, forming glycation wrinkles and premature aging.

Electron spin resonance (ESR) is an in-vitro test method whereby an electron trap is used to prolong the life of radicals generated by exposure to solar-simulated radiation which makes the detection of the radical species easier.

Experiments were conducted using ESR to assess the numbers of radicals generated with and without a formulation (containing a UV filter) present on a skin substitute. The studies show that 25% of the free radicals generated in the UV/Visible region of the solar spectrum derive from the HEV portion of the spectrum. When a filter protecting from HEV, such as a non-nano titanium dioxide is used, a 75% reduction in the amount of free radicals generated was found. This demonstrates the shielding effects of such a filter and benefits of protecting the skin from HEV (2).

Further along the solar spectrum, past the visible region, is the Infrared (IR) region, which is electromagnetic radiation with longer wavelengths than visible light, therefore rendering it invisible to the human eye. Whilst IR is not visible, it is extremely prevalent in daily life, with 54% of the sun's radiation being IR (3).

The latest research on this topic comes from Newcastle University, UK. They have completed a study to evaluate the effects of different components of sunlight on cells from the Dermis (fibroblasts) and skin equivalents and the generation of Reactive Oxygen Species (ROS), which are known to contribute to oxidative stresses, a factor of aging. They found that, using skin cell lines, there was a greater induction of ROS, mitochondrial DNA, and nuclear DNA damage with the inclusion of the visible and IR components of solar-simulated light in primary fibroblast cells compared to primary keratinocytes ($P < .001$). Furthermore, experiments using exposure to specific components of solar light alone or in combination showed that the UV, Vis, and IR components of solar light synergistically increased ROS generation in primary fibroblasts but not primary keratinocytes (4).

The harmful effects of IR are just starting to be addressed in the market with products offering IR protection starting to become more prevalent.

To address this market for IR shielding actives, Croda have developed a large particle size titanium dioxide based physical shield that offers instant protection from IR rays. This product is based on patented dispersion technology which ensures that, despite the large particle size, it has minimal whitening on the skin, making it the ideal active to add to skin and sun care UV protection products to deliver guaranteed IR protection claims.

So, if the question is; is conventional UVB and UVA protection the most important aspect of a solar protection product then yes it absolutely is, however, if the question is; should we also look to expand BEYOND UV protection then the answer is a resounding YES.

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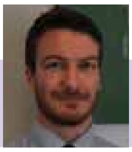

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DOES IT MAKE SENSE TO PROTECT FROM BLUE LIGHT, VISIBLE LIGHT OR INFRARED LIGHT?

BACKGROUND

According to the FDA, exposure to the sun can cause sunburn, skin aging, eye damage, and skin cancer (1). The High Energy Visible Blue Light, HEV (400-450 nm), other Visible, VIS (450-700 nm) and Near Infrared, NIR (700-1100+ nm) are increasingly recognized as contributors to skin photodamage. Duteil L. et al. demonstrated that Blue Light induces a long-lasting hyperpigmentation that was more pronounced versus UVB-induced (2). Melanocytes sense these wavelengths directly through the activation of a specific sensor Opsin-3 (3). Human skin irradiated with Blue Light shows a light - dose - dependent degree of pigmentation (4).
The exposure to VIS and NIR from natural sunlight upregulates matrix metalloproteinases MMP-1 and MMP-9 expression in skin, and decreases Type I procollagen synthesis (5).

THE OUTDOOR EVALUATIONS OF SOLAR IRRADIATION

Florida, the "Sunshine State", is closest to the equator in the continental United States and receives high levels of sunlight. Intellebio, LLC conducted the outdoor evaluations of solar irradiation in Vero Beach, Florida (27.6386° N, 80.3973° W) on March 23, 2021, at clear sky; measurements were conducted every hour, from 12 (noon) till 4 PM EDT. Several Solameters®, compact devices with traceable accuracy, all from Solar Light Company, Inc. (6) were utilized to simultaneously assess the irradiation in the spectral areas of interest:

- **4.0 UVA:** 320-400 nm; irradiation range 0-199 mW/cm²; peak response at 370 nm;
- **5.0 Total UV (A+B):** 280-400 nm; irradiation range 0-199 mW/cm²; peak response at 370 nm;
- **6.0 UVB:** 280-320 nm; irradiation range 0-19.99 mW/cm²; peak response at 300 nm;
- **7.0 MED/hr:** 280-400 nm; erythemally weighted UV; range 0-199.9 MED/hr;
- **9.4 Blue Light:** spectral response 432-499 nm; irradiation range 0-199 mW/cm²; peak response at 450 nm;
- **10.0 Global Solar Power Meter (Visible + Near IR):** spectral response 400-1100 nm; irradiation range 0-1999 W/m²; peak response at 960 nm.

During measurements these instruments were aimed at sun to record the maximum irradiation intensity.

The experimental data are presented below:

Time, EDT	Solameter® Type					
	4.0	**5.0**	**6.0**	**7.0**	**9.4**	**10.0**
	mW/cm²	mW/cm²	mW/cm²	MED/hr	mW/cm²	W/m²
12 PM	4.8	5.2	0.28	5.2	12.5	960
1 PM	4.9	5.8	0.32	5.8	13.5	975
2 PM	5.3	5.6	0.31	5.7	12.1	947
3 PM	5.1	5.4	0.26	4.8	11.9	936
4 PM	4.5	4.7	0.18	3.1	10.9	920

The highest intensity of sun's rays was observed in all tested spectral regions at 1 PM EDT, not at 12 PM (noon) - due to the change to the daylight-saving time. The MED/hr and relevant UVB flux values decreased significantly from 1 PM to 4 PM. These data indicates that even at the beginning of Spring in Florida, there is still high to moderate risk from unprotected sun exposure. In comparison to the UVB irradiation trend during same period of time, the intensities of UVA, Blue Light and VIS+NIR were decreasing to less degree, from 5.3 to 4.5 mW/cm²; 13.5 to 10.9 mW/cm²; and 975 to 920 W/m², respectively.

BLUE LIGHT FROM NATURAL SUN VS. ELECTRONIC DEVICES

Comparison of Blue Light flux densities in 420-490 nm range emitted by electronic devices and by the sun indicates that the ratios between the intensity of the sun VS. intensities of several devices (e.g., TV LED, laptops, computer screens and cell phones) in this spectral region vary from 99 to 1069 (7). According to Unilever, 60% of people now spend more than six hours a day in front of a digital device which, when spread across five working days, equated to the same impact on the skin as spending 25 minutes in midday sun without protection. Blue Light emitted from screens can induce both immediate and persistent pigmentation, inhibit melatonin generation, increase stress hormone levels and excite nerves, which can disturb sleeping patterns and circadian rhythm. Consumers who are exposed to 30 hours of Blue Light from a smartphone or laptop screen can increase their inflammation level in skin cells by 40% (8).

INGREDIENTS AND FORMULATIONS

In 2018, Dueva-Koganov demonstrated that mineral non nano sunscreen actives (ZnO alone or with TiO_2), also in combination with organic sunscreens (e.g., Tinosorb M and Tinosorb S), particulate materials (e.g. silica, talc), and iron oxides contribute to sunscreen's improved protection against Blue Light. Proposed Blue Light/UV Ratio was utilized as a new metric to compare sunscreen's protection potential in this region (9). Kobo indicated that coated TiO_2 with~35 nm primary particle size can effectively block Blue Light; and transparent red iron oxide used at a very low level was shown to neutralize the whitening/bluing associated with higher TiO_2 use level; 40% or more of Blue Light attenuation can be achieved by easy-to-use dispersion TPN45TELR (10). Two grades of micron range TiO_2-IR-300 and A1K-TiO_2 effectively attenuate IR, and impart thermoprotection to the skin in vivo (11). Color correcting filler RonaFlair Balance Blue provides Blue Light mitigation (12). Unilever suggests consumers to use products with the following ingredients in order to protect themselves against Blue Light-induced skin damage: optics, which minimize Visible Light to prevent skin tanning; ZnO, mineral sunscreen active; Vitamin C; Vitamin B6 and Niacinamide (8).

PATH FORWARD

Arguably, the spectral range from 290 to 1100+ nm is the most biologically relevant. In addition to the established effects of UV radiation, Blue Light, VIS, and NIR parts of the solar spectrum also contribute to skin photodamage. Unilever said it was on a mission to help people 'beat the screen blues' by raising awareness of the negative impact Blue Light has on skin (8).

It should be noted that the intensity of Blue Light emitted by the sun is approximately 2 to 3 orders of magnitude greater VS. electronic devices. The experimental data provided above re-enforces the importance of comprehensive sun protection in UVB/UVA, Blue Light, VIS and NIR regions. The development of multifunctional sunscreen formulations capable of providing measurable protection beyond UV is a challenging task that requires the development and utilization of specialized ingredients and formulations (4, 8-12), and relevant testing methodologies and metrics, e.g., Blue Light/UV Ratio (12).

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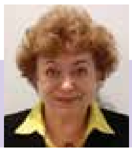

SUN PROTECTION METRICS: GOLD STANDARD, REFERENCE AND ALTERNATIVE METHODS

The biological/clinical phenomena of erythema caused by natural or simulated solar radiation and photooxidation of melanin by simulated UVA radiation in humans have led to the development of two ISO standardized methods (ISO 24444, ISO 24442) used to characterize the performance of sunscreen products (Sun Protection Factor (SPF), and UVA Protection Factor (UVA-PF)). Both in vivo methods - today mostly referred to as gold standards - expose volunteers to potentially harmful radiation and their usage is complex, time and cost intensive. Efforts were made early on to develop alternative, easier to handle methods. These efforts to search for alternative methods were only recently additionally reinforced when it was reported that significant inter-laboratory variance in the measurement of the $SPF_{ISO\ 24444}$ exists (1). The cause of these variations has not yet been systematically addressed. From experience with other methods, it is believed that skin surface characteristics, equipment, laboratory staff and/or sunscreen vehicle formats and vehicle ingredients could be the cause (2, 3). So far there are no such studies for the determination of $UVA\text{-}PF_{ISO\ 24442}$. As manufacturers of sunscreen products or consumer protection organizations contract various research organizations to determine the $SPF_{ISO\ 24444}$, the observed inter-laboratory variance raises questions concerning the reliability of the claimed SPF on the sun protection packaging and the verdicts of the consumer protection organizations on unmatched SPFs particularly when based on a single determination in only one laboratory (1). There are a number of methods that may serve as alternatives and/or have the potential to complement the gold standards, to serve as equivalents or even to replace them in the future. Well known examples for labels derived from alternative methods are the circle with UVA (EU) (UVA-PF/SPF>0.33), additional specifications such as "broad-spectrum protection" (critical wavelength) (US, EU) or "star rating" (UVA/UVB ratio) (UK). A UVA1/UV ratio > 0.7 is proposed as a pass/fail criterium in the US.

The alternative methods are based on a) the *in vitro* measurement of UV radiation transmittance through a sunscreen film spread over a substrate (e.g., roughened PMMA-, quartz plate), b) the in vivo measurement of diffuse reflectance (diffuse reflectance spectroscopy: DRS) (double-transmittance) on human skin covered with a sunscreen film, and c) the in-silico calculation of transmittance.

The relevant literature has shown that in the context of sun protection metrics, terms such as gold standard, reference and alternative methods, validation or equivalence testing and fit-for-purpose are either understood differently or used inconsistently (4-8). In the following the terms are circumscribed more precisely. A gold standard method may refer to an experimental setup that has been thoroughly tested over a longer period and has a reputation in the field as a reliable method - in short, the best available method. This applies, for example, to the determination of the SPF, which has been internationally harmonized since 1994 and globally standardized by ISO since 2010. Where the gold standard method is used to assess another, alternative method, the gold standard method becomes the reference method. To replace a gold standard method (or reference method) with a new method (or alternative method), some sort of equivalence testing is necessary. A prerequisite for equivalence testing is the suitability (validity) of both methods to determine defined and corresponding parameters (e.g., the same radiation spectrum). Validation of a method (suitability testing) is a defined process designed by the user/beneficiary in which they define the criteria for its suitability for an intended purpose ensuring an adequate level of discrimination (fit-for-purpose). A comprehensive characterization of the methods is a prerequisite for initiating the validation procedure. In other contexts, the term validation is used as an act or process to make something officially or legally acceptable or approved. It is important to note, that such an interpretation of the term would be misleading without a prior formal mandate from a competent body.

The term validation is also used as a synonym for terms such as assessment, evaluation or appraisal. Once the validation of methods has been successfully completed, their equivalency can be assessed. As in the case of the validation, the users/beneficiaries define the criteria (fit-for-purpose) that demonstrate the equivalency for the methods. The term fit-for-purpose includes the acceptance criteria and emphasizes that these have been specified by the user/beneficiary to fulfil the intended tasks. As in other disciplines (e.g., laboratory medicine), all participants from the field of the topic presented here should agree on a mutually accepted use of terminology.

Several approaches have been used for evaluating equivalency. The correlation coefficient is not suitable to evaluate equivalency (agreement) between two methods because the correlation coefficient will automatically increase (improve) the further the value pairs are apart. The Bland-Altman approach is sufficient to demonstrate equivalency of methods, however product and laboratory effects are not properly distinguished with this approach (9- 11). The ISO 5725 standard offers basic guidance regarding the estimate of method precision. However, the models in ISO 5725 are intended to be applied to one single product. Uhlig et al. proposed a special experimental design and statistical model which will yield estimates of both trueness and precision and allow a representative number of different products (i.e., in relation to the alternative method's scope) to be included in the investigation (12-14). The experimental design – referred to as an orthogonal factorial design – allows a reliable estimate of trueness and precision even with a reduced number of participating laboratories. Such designs have been described in several articles and in the new ISO 16140 series (parts 4 & 5) for method validation in food microbiology; they will also be described in the revision of ISO 5725-3 (15-17). The orthogonal design will be applied in a suitability investigation initiated by a recently inaugurated initiative (Consortium ALT-SPF) (18). Their aim is a) to demonstrate the value of the alternative methods against the Gold Standards and b) to demonstrate their future use for a more comprehensive characterization of the protective performance of sunscreen products - a benefit for both the consumers and the developers. Once suitability has been demonstrated, the additional capabilities of the newly assessed alternative methods can be exploited.

The potential of alternative methods lies in their capability to generate statements and extended claims about a product's protection performance that go beyond the statements that are based on the radiation spectra as used in $SPF_{ISO\ 24444}$ or $UVA\text{-}PF_{ISO\ 24442}$ – e.g., UVA1, blue light, visible light or infrared light. In fact, alternative methods (based on transmittance) allow to calculate the protective performance of a product for each wavelength (monochromatic protection factor (mPF)) (19). In the same way, the protection against any radiation spectrum including the spectra used in the gold standard methods can also be calculated – the latter being prerequisites for testing the suitability and equivalency of alternative methods compared to the reference methods. Nevertheless, one should be aware that both the Gold Standards and the alternative methods cannot fully depict the real situation correctly. The Gold Standards are a reflection of a biological effect, while the alternative methods provide information based on the simulated or natural solar radiation spectra and specific action spectra (e.g., erythema, skin cancer, elastosis) and transmission data (20). With the Gold Standard methods, the sun protection products (format, filters, vehicle ingredients etc.) are applied to the human skin like in real life. This is not the case when applying to substrates.

Once suitability and equivalency between reference and alternative methods have been established, any of the methods - individually or in combination - can be - comparable to tools from a toolbox - used to reliably assess a more holistic protection performance of sunscreen products. Such methods complementing each other would be a significant step forward for the development and utilization of sunscreen products.

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UNDERSTANDING SUNSCREEN PRODUCTS TESTING METHODS. HOW WILL THE LEVEL OF PROTECTION BE DETERMINED IN THE FUTURE?

The introduction of the first measurement system against solar radiation in the 1930s represents an important milestone in the determination of the level of sun protection in the 1950s. The term SPF first appeared in the 1960s and around 1978 the SPF number started to be included on the product label as well.

Currently we still continue to classify sunscreen protection with a numeric SPF. However, we have a better understanding of the importance of sun care and consumers are becoming more knowledgeable and require transparency and safety. Beside this, the industry is evolving towards new horizons.

SPF is a representation of the defense against UV, combining efficacy and safety. This is because determination of the sun protection level translates to safety against long exposure. The benefits include protection against sunburn, photoaging and skin cancer prevention, amongst many others.

The starting point to evaluate each sunscreen product is through the traditional gold standard ISO 24444 (or the similar FDA method). The first edition of this procedure: ISO 24444:2010 has recently been replaced by the second edition ISO 24444:2019.

The main differences in the procedure lie in improving the quality of products and the method reproducibility due to high variability. Some of the main changes include:

- Selection of the test subjects by colorimetric determination of skin color, using ITAº value for skin type classification. An average ITAº value is required and the subjects included must be fit within different ITAº ranges.
- New standard sunscreen formulations with SPF references P5, P6 and P8 have now been included.
- Sunscreen application procedure description in greater detail.
- Definition of the minimal erythemal response (MED) and visual guidance for erythema grading.
- Determination of the beam uniformity, greater than or equal to 90%, has been added.

Honestly, the ideal result of this procedure is to get an SPF value greater than we had initially expected for the labelling. To a certain extent, this would compensate for the insufficient product quantity that final consumers tend to apply.

It is important to bear in mind that the ISO 24444:2019 is still under development and the industry expects a first amendment soon.

Another standard study is the evaluation of the UVA protection using in vitro methods; ISO 24443:2012 that specifies the procedure to characterize the UVA protection of sunscreen products or in vivo determination of the UVA protection by ISO 24442:2011, both under development and expected to be replaced.

As to secondary claims, the latest standard methods to evaluate water resistance follow the ISO 16217: 2020 guidelines (Water immersion procedure for determining water resistance) and ISO 18861: 2020 (Percentage of water resistance). In terms of equipment, this method requires a special bathtub with a flow, conductivity, pH and temperature control.

As people's lifestyles have been changing with time, researchers and organizations are now developing and improving methods focused on evaluating others claims in order to get the ideal sunscreen product.

There has been an increase in the amount of research on the effects of other skin radiations in the recent years. Nowadays, most of these studies include evaluation of oxidative stress, inflammatory cytokines, blue-light damage protection and expression of MMPs. Other claims such as sweat resistance and sand resistance do not follow standard guidelines. Nevertheless, these claims may be more investigated and regulated in the near future as the industry might develop international guidelines to harmonize these methods worldwide.

Regarding the testing methods, efforts from the industry are focused on non-invasive and more ethical in vivo testing alternatives that would be easily adaptable by all laboratories.

In conclusion, the future of sunscreen products could be the creation of multifunctional products that would offer protection against radiations at different levels. These include numeric Sun Protection Factor, UVA Protection Factor, Blue Light Protection Factor or IRA Protection Factor further supported by water or/and sand or/and sweat resistance. Apart from improved formulas, we are also very likely to see introduction of new technology and devices that would allow us to monitor product application and re-application quantity and times.

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SUNSCREEN IMPACT ON ENVIRONMENT

SUNSCREEN FILTERS AND ENVIRONMENTAL EFFECTS

With over 4,000 tons of sunscreens washing off into the world's oceans each year (1), increasing scientific interest on the impact of UV filters in the environment, particularly in coral reef ecosystems, has spilled over into the consumer and political arenas. Much of this attention has focused on organic UV filters, which were first hypothesized in 2008 to have toxicological effects on coral reefs (2). This has subsequently led to recent legislations enacted in some tropical regions, including Palau, Bonaire, Aruba, U.S. Virgin Islands and Hawaii, that prohibit the use of select UV filters, oxybenzone and octinoxate, with more bans being considered globally.

At the same time, sunscreen has become an integral part of our photoprotection strategy to combat skin cancer and photoaging. Both organic and inorganic UV filters have found their way into more products to provide everyday sun care protection. Additionally, consumer's desire to use higher SPF products has also led to an increase in the use of UV filters that could potentially make their way into the environment.

As regulations continue to restrict the use of sunscreen ingredients, attention has begun to focus on zinc oxide (ZnO) as the UV-filter of choice when developing reef-friendly sunscreens. Such attention has also brought about misinformation in the public domain of the true environmental impact of ZnO. Therefore, it has become even more important to provide a balanced view of the impact of ZnO and other UV filters on coral reefs so consumers can make informed choices in their buying behavior. As a trusted zinc oxide supplier, EverCare commits to fully understand and present the real impact of UV filters, especially zinc oxide, on aquatic life in general and particularly on corals through our Positive Reef Initiative.

With coral reefs disappearing at alarming rates, the significance of protecting these natural wonders cannot be understated. As such, EverCare has introduced its Positive Reef Initiative to actively contribute to influencing coral reef restoration. Through three focused pillars, the Positive Reef Initiative is committed to helping consumers make informed decisions on their sunscreen purchases, to researching and restoring coral reef populations, and reducing our global carbon footprint to reduce our impact on climate change, which affects coral reef habitats. With increased awareness of the impact of sunscreen on coral reefs, consumers are not only looking for natural, reef-safe ingredients for their sun care products, they are also looking for brands committed to protecting the environment.

EverCare is dedicated to understanding our products and their impact on the environment for consumers to be able to make smart purchases when choosing their sunscreens. In our view, this starts by understanding the true impact of our ingredients on coral reefs and presenting a balanced view to empower consumers to make informed choices. The key to achieving this balanced view is to move from a hazard profile to a risk and exposure scenario to look at the actual impact that different products have on the environment.

EverCare commits to fully understand and present the real impact of UV filters, especially zinc oxide, on aquatic life in general and particularly on corals.

As researchers continue to investigate the impact of sunscreen ingredients on coral reefs, it is well established that the major threat to coral reefs globally is changing climate conditions. The Positive Reef Initiative is committed to supporting the development of science on damage and reef restoration as well as supporting the active reef restoration itself. Through a unique partnership with Love the Oceans, a non-profit marine conservation organization, several programs have been started with aims to successfully repropagate coral reefs in the Mozambique coastal region that has been significantly impacted by weather events in the past years.

The Positive Reef Initiative is a long-term commitment to support the use of safe sunscreen ingredients and make a positive impact on the environment. While science will continue to evolve and shape regulations, we can proactively work to put in place and support research programs that help the proliferation of healthy coral reefs that in turn have a positive influence on the local community of these habitats, both socially and economically.

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SUNSCREEN IMPACTS ON MARINE LIFE: CHALLENGES AND FUTURE PERSPECTIVES

The oceans represent the largest biosphere on the planet. Over 95% of life is underwater, and the enormous biodiversity of the seas and oceans is an inestimable source of goods and services that support human beings. However, the intense exploitation of its resources, pollution and climate change are altering its integrity. The United Nations, international economy strategies and the European Union consider the health of the oceans a priority of global importance for the sustainable development of our planet. The development of a One Health approach, where healthy oceans and seas tightly linked to human health, appears a priority for the sustainable future of the Planet.

Among the thousands of contaminants released in the sea, there is increasing evidence that sunscreens despite their extremely low concentrations can have disproportionately high impacts on a large variety of aquatic organisms. Consequently, the ban for some ingredients such as the octinoxane and oxybenzone is planned or already adopted in several countries. In the future, the ban could be extended to other cosmetic ingredients (e.g., parabens), following actions already adopted by several resorts and parks in Florida, Mexico, the Virgin Islands and the Republic of Palau, Maldives and in other countries in the world.

Although tropical coral reefs are amongst the most fragile and vulnerable habitats to sunscreens, there is increasing evidence that sunscreens can affect most organisms from the tiny phytoplankton to large fish. For example, oxybenzone and homosalate can cause alterations in the development of the sea urchin causing abnormalities in its embryos and larvae and other components such as enzacamene and preservatives (parabens) cause coral bleaching. The list of harmful ingredients could soon include also fragrances and other excipients on which tests are being performed.

Although organic filters dominate the sunscreen market, the use of inorganic filters such as zinc oxide and titanium dioxide is widely spread, because they represent an alternative to chemical filters and provide a broad spectrum of protection to our skin against UV rays. However, recent studies conducted in the Mediterranean Sea are showing that also these compounds, once released into water, can generate reactive oxygen species, can release toxic metals and have deleterious effects for marine organisms.

Filters such as titanium dioxide and zinc oxide have also been found to be harmful to corals and their symbiont algae. Furthermore, titanium dioxide and zinc oxide in form of nanoparticles are extremely harmful to sea urchins, crustaceans, stony corals and microalgae due to their ultramicroscopic size, which allows them to be incorporated into the organs and tissues of marine organisms causing cell damage and cytoskeletal alterations, especially in their larval and juvenile forms. The chemical form and characteristics of the inorganic filter can also modulate the effects on marine organisms. Recent studies have revealed that especially ZnO nanoparticles are harmful to corals, while TiO_2 coated and metal doping has a much lower impact.

To overcome these limits and to achieve the objectives of the ocean and human health, it is urgently needed to develop a strong cooperation between the industry and marine research, in order to include multidisciplinary skills in the fields of cosmetic, cosmeceutic, dermatology, cell biology and marine biology and ecology. This new "alliance" is the only sound solution to develop the eco-sustainable sunscreens of the future, offering an enhanced skin protection, while preserving at the same time a healthy marine life.

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MEETING CONSUMER EXPECTATIONS

IDEAL SUNSCREEN FOR NEW ROUTINES

HABITS – THE NEW OUTDOOR

With the COVID-19 pandemic and strict lockdown in place, consumers are prioritizing outdoor activities and are longing for their next holidays, as these are essential to one's mental well-being. As these activities return, this also means people will experience greater exposure to the sun's rays.

Although most consumers are well aware of the damage caused by inappropriate sun exposure, changing one's habits can still be a challenge. Though people usually remember to pack a sun cream when going out for holidays, applying it when gardening, having lunch outside, or teaching kids to remember it when playing in the schoolyard is another story.

Consumers are also paying more attention to their impact on their surroundings. They are looking for products that are safe for their health and safe for the planet. To ensure they are well protected from the damages of the sunrays, developers of new technologies must ensure consumers will enjoy applying the product as this will increase the likelihood that they reapply often enough to ensure a good protection. This can be achieved via sun care products in attractive formats with appealing textures that are suitable for all skin tones and create strong sensorial emotions.

PROTECTING OUR PLANET – PROTECTING OUR HEALTH

In response to the desire for product safety and transparency, Dow has developed a brand-new
bio-based and readily biodegradable SPF Booster that enables greater SPF efficiency in sun care and daily skin care. Derived from Programme for the Endorsement of Forest Certification (PEFC)-certified wood pulp, Dow's new innovative microcrystalline cellulose supports the market demand for natural formulations.

This ingredient delivers various benefits beyond SPF boost including thickening and shear thinning behavior, helping the formulator achieve new formulation formats with a pleasant sensorial experience and better naturality.

The innovative microcrystalline cellulose works with organics, mineral sun filters, or a combination of both, while helping to reduce the level of emulsifier thickening agents that could be in formulator disaffection. Utilizing this ingredient helps support the market demand for naturally sourced formulations that are safe for the environment. This unique SPF booster demonstrates *in vitro* and *in vivo* SPF boosting performance.

DIVERSE SKIN TONES - DIVERSE FORMATS

Formulators and marketers are constantly looking for innovative formats that support multifunctional products, new creative galenic, and trends like genderless solutions or products that fit all skin tones.

Traditional silicone-based technologies have enabled high SPF and broad-spectrum protection for daily-wear SPF anti-aging products designed for pale to medium skin tone consumers, but have yet to be leveraged to their full potential for a more diverse set of consumers. While silicones are known for their improved aesthetics and SPF enhancement, reduced whitening and ashiness on all skin tones, including darker skin types, is critical to ensure compliance of sunscreen with the increased usage of physical blockers such as TiO_2 and ZnO.

Silicone emulsifiers, such as the silicone glycerol emulsifier, play an important role in decreasing whitening on the skin and are shown to be effective at a very low level in formulating sun protection products. Physical sunscreens formulations with a lightweight feel can help to meet the growing demand for multi-performance cosmetic products, particularly BB and CC creams.

Well-being is part of the total sun care experience and creating galenic, transparent, gel-like textures with unique sensorial feel is possible with technology like silicone hydro elastomer gel. This elastomer gel maintains texture at high water or glycerin levels and is compatible with a wide range of organic ingredients, including sun filters, allowing the creation of clear gel, while delivering a fresh and silky feel for a unique sun care experience.

NEW ROUTINES – NEW FORMATS - NEW SOLUTIONS

Addressing new consumer routines and diverse preferences in terms of formats, such as on the go formats or gel textures, is a way to drive further usage of sun care products and enhance skin protection against the adverse effects of UV Rays.

Developing technologies such as Dow's innovative microcrystalline cellulose or sensorial additives that enable attractive and pleasant textures and excellent spreading on the skin without whitening effects is the right path to boost sun care products' adoption with diverse consumers, including men who tend to have a much lower usage than women.

New solutions that meet the performance level expected by consumers and are safe to the planet and ocean will alleviate consumers' concerns over sun care products, while enticing them to better protect their skin.

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ARE SUNSCREENS BLOCKING THE BENEFICIAL ASPECTS OF SUN EXPOSURE?

There is no dispute that UV radiation is the prime cause of various skin cancers, including melanoma, the deadliest form. The exact circumstances under which UV causes melanoma to evolve may not be fully understood, but non-melanoma skin cancer shows a clear localized preference for the most exposed skin areas, e.g. nose, ears, and hands. Protecting against UV light – by seeking out shade, covering exposed areas with clothing, and using sunscreen – is recommended as a prime tool in inhibiting skin cancer formation.

Although nowhere near as invasive as cancer, the aging effects of sunlight are quite socially relevant, nonetheless. Both UVA light and blue light emitted by the sun penetrate deep into skin, causing oxidative stress. This then permanently damages elastic tissue, resulting in the appearance of photoaging phenomena such as wrinkles. Physical protection in the form of a sunscreen also makes sense in this context, lowering the impact on skin tissue to preserve a younger looking appearance.

In all circumstances, the use of sunscreen requires a degree of tolerance towards applying a somewhat greasy product, even though significant progress has been made in minimizing this issue (1). And not every consumer is willing to use sunscreens, as our recent survey (2) in 2018 showed. About 20% of consumers worldwide do not use sunscreens at all, and a considerable number of consumers only use sunscreen on specific occasions, leading to unprotected exposure when they have not planned to go into the sun.

The inherent benefits of sun radiation are often cited as a reason for intense exposure. And one benefit in particular seems to be the main driver: Sun light enhances our mood. This happens via different pathways, due to the brightness perceived by our eyes and skin acting on light like a sensor for the brain. A couple of molecular reasons, dependent on different light sources and biological channels, have also been elucidated (3). Communication about protecting against skin cancer needs to take this into account, otherwise the advice to protect is simply perceived as "fun inhibition", and ignored.

There are clear benefits to sun exposure, but they often run concurrently with the hazards, and so require careful dosage control. The benefits usually require much less than 1 MED radiation to take place. UVB light not only causes direct DNA mutations in skin cells but also initiates Vitamin D synthesis (4). Additionally, it upregulates the local neuroendocrine axis to set up mood enhancement, as does blue light (5), which is usually not absorbed by sunscreens at all. UVA light causes Nitric Oxide formation in skin (6), indeed, skin seems to be the largest body reservoir of NO-precursors. NO reduces blood pressure, but on the other hand, it is also a potentially risky oxidant, which has not yet been well studied. UVA causes immediate skin tanning and UVB delayed skin tanning, and in the western hemisphere, at least, this is a fashion target. In France, the desire for a suntan drives consumers to unprotected UV exposure. In contrast, in Korea or Japan, where the fashion target is to avoid skin tanning, consumers adhere scrupulously to sunscreen usage. UV light also has many therapeutic applications for skin conditions such as psoriasis, vitiligo, atopic dermatitis and localized scleroderma(6), but those treatments happen under controlled conditions, in particular the dosage of UV is fully supervised.

So can sunscreens block all the beneficial aspects of UV exposure and are all the sad people on the beach feeling sad because they use sunscreen? Definitely not! In general, sunscreens are underapplied and this reduced use level also reduces protection factors against UVB and UVA light. The protection factor for UVA is, in any case, typically three times smaller than for UVB. This is regulated by the claim makers. With a use level of 0.4 mg/cm^2 for example (7), in practical terms, we can expect an SPF 30 lotion to achieve an SPF of just 6 at the beach. This is just enough to prevent serious sunburn, but after a full day's exposure, e.g. on a sunny day on the French Rivera, it is not high enough to prevent 1 MED being received through the sunscreen film. This degree of redness, which consumers typically call "a little red" is not tremendously painful and exposure can continue the next day. Such a consumer will have received a strong dose of UVB and UVA in addition to a high amount of visible light, generating all the benefits mentioned above in abundance. The sunscreens will have offered some protection – although at 1 MED level, not enough to reduce skin cancer– and benefits such as Vitamin D synthesis (8), mood enhancement, and tanning will still manifest, despite sunscreen use.

Clearly, there is room for greater protection against skin cancer while still receiving the benefits of sun exposure at an adequate level. Practically, and by not changing consumer behavior by being "fun busters", we need to get in-use-SPF levels during sunbathing to at least 10 to see some impact on skin cancer incidence. This would enable everybody to still enjoy a sunny holiday and to come back with a full Vitamin D reservoir and a relaxed blood pressure status.

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UNDERSTAND CONSUMER EXPECTATIONS TO FORMULATE EFFICIENT SUNCARE PRODUCTS

After years of risky behaviour, consumers are more aware that it is highly important to use an efficient sunscreen to avoid bad sun effects. But they expect it to be pleasant to use and they want to get tanned.

Facing with increasingly demanding consumers, the market has diversified, to the detriment of formulators for whom the formulation of suncare products has become a real headache.

CONSUMER EXPECTATIONS HAVE CHANGED

Efficacy comes first. But it is not only linked to the performance of the product. Indeed, an efficient sunscreen is a sunscreen that is functional, pleasant to use, easy to apply and reapply and that suits consumer needs.

New claims emerged. Skincare claims have been invited on the packaging of suncare products: moisturizing, soothing, glow, anti-aging, anti-pollution, antioxidant, firming... Functional claims also appeared, like: tan activating, sand resistance, water resistance or clothing protection. Finally, green claims are more and more adopted: ocean/reef safe, biodegradable, natural, mineral (mineral filters are perceived as safer by a growing number of consumers).

There are now varied galenics to satisfy all desires and make suncare easy and fun to use: cream, lotion, spray, stick, mist, mousse, bi-phase, solid form, roll-on.
So, how to suit consumer needs while ensuring the product is efficient?

IMPROVE THE PERFORMANCE

Above all, a suncare product must be efficient. The first thing to check is that UV filters are well solubilized or dispersed in the formula to guarantee a homogeneous protective film. Each organic filter has its optimal solubilizer, so an experimental lab work is needed to make the right choice (visual test, microscopy). Supplier's information is also a great help. Regarding inorganic filters, the best option is to choose coated grades that improve compatibility, dispersibility and sensoriality compared to uncoated ones. The choice of the coating is also essential according to the oil phase since it must be compatible with it to avoid any instability problem.

Another tip is to combine organic and inorganic filters to take advantage of the synergy effect. As their mechanisms of action and absorption spectrum are different, the final product will be more complete and then efficient in any situation.

Finally, performance is not only linked to UV filters used but can also be improved by additional ingredients. For example, photostabilizers are a great help to maintain UV filters performance over time, especially UV radiation. Film formers are also useful to maintain a homogeneous film at the surface of the skin that is water-resistant.

IMPROVE THE STABILITY

Stability issue is frequently observed in suncare products, because of their complexity in terms of composition. To improve it, stabilizers such as gelling agents have to be carefully chosen, especially regarding the final form, depending on their thickening and stabilizing capabilities and their thixotropic effect.

Another thing to keep in mind is the choice of the emulsifier. It has to contain a low fatty alcohol content, especially if the final form is a thick cream. Indeed, under the effect of heat, fatty alcohols melt and then the formula become fluid and may lead to destabilization.

IMPROVE THE SENSORIALITY

Finally, sensoriality is a key factor to ensure that the product will be appreciated, applied and reapplied and therefore effective. But formulating a sensorial suncare product is not an easy task. Organic UV filters bring greasiness, a high film residue and tackiness. Inorganic UV filters bring dryness, roughness and a whitening effect especially if they are not in nano form. At last, a high amount of oil phase is needed to solubilize or disperse UV filters, that can lead to a greasy and heavy afterfeel.

Some solutions exist. The first thing is to vary the emollients to find the right balance between UV filters compatibility and sensoriality. The use of feeling agents like powders is also a good option to reduce the greasy and tacky effect. Use SPF boosters will help to reduce the total amount of UV filters and then oil phase. Changing the emulsifier could be relevant as this compound tends to have a sensory impact on the final formula. Finally, using inorganic filters with a smaller particle size is a way to reduce the whitening effect during application.

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